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SO_2-induced stability of Ag-alumina catalysts in the SCR of NO with methane

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ABSTRACT

We report on a stabilization effect on the structure and activity of Ag/Al_2O_3 for the selective catalytic reduction (SCR) of NO_x with CH_4 imparted by the presence of SO_2 in the exhaust gas mixture. The reaction is carried out at temperature above 600 °C to keep the surface partially free of sulfates. In SO_2-free gases, catalyst deactivation is fast and measurable at these temperatures. Time-resolved TEM analyses of used samples have determined that deactivation is due to sintering of silver from well-dispersed clusters to nanoparticles to micrometer-size particles with time-on-stream at 625 °C. However, sintering of silver was dramatically suppressed by the presence of SO_2 in the reaction gas mixture. The structural stabilization by SO_2 was accompanied by stable catalyst activity for the NO reduction to N_2. The direct oxidation of methane was suppressed, thus the methane selectivity was improved in SO_2-laden gas mixtures. In tests with high-content silver alumina with some of the silver present in metallic form, an increase in the SCR activity was found in SO_2-containing gas mixtures. This is attributed to redispersion of the silver particles by SO_2, an unexpected finding. The catalyst performance was reversible over many cycles of operation at 625 °C with the SO_2 switched on and off in the gas mixture.

1. Introduction

Silver catalysts have found unique application to ethylene epoxidation [1,2] and hold great promise for the SCR of NO_x with hydrocarbons [3,4]. However, sintering is a serious issue for silver catalysts [5–10], and a complex array of factors have been linked to sintering, including the reaction gas environment [7,8], support effects [11], and surface binding and mobility [12]. Insights into silver growth and agglomeration mechanisms have been gained primarily from investigations of model silver catalyst systems, such as Ag films [5,6] and model Ag-alumina systems [7,11,13]. Presland et al. [5,6] have observed agglomeration of silver on annealing a silver film in oxygen, which was accompanied with the formation of hillocks and pits. It was proposed that silver migrates via surface diffusion which is enhanced by the presence of oxygen [14–17]. The appearance of big Ag clusters was found at much lower loadings than Mn on $Al_2O_3/Ni_3Al(1\,1\,1)$ surface by STM [13]. Bird et al. [11] investigated the growth of silver on model Ag-alumina catalysts by AFM (atomic force microscopy), and found that the structure and stability of silver deposits have a strong dependence on the crystalline structure of alumina. Ruckenstein and Lee [7] performed an extensive microscopy study of the sintering behavior of model Ag/Al_2O_3 catalysts in O_2, C_2H_4 or C_2H_4/O_2, and found that the stability of silver depends strongly on the reaction gas environment.

Using DFT, Meyer et al. [12] examined silver bonding to various Al_2O_3 surfaces, and found that stronger bonding exists with the O-terminated than with the Al-terminated surfaces. As a consequence, the diffusion barrier for silver is higher on the former surface than on the latter. The strength of Ag bonding to hydroxylated alumina surfaces was calculated to be intermediate between O-terminated and Al-terminated surfaces. Similar to the above model catalysts, Seyedmonir et al. [8] found that for supported silver catalysts, silver sintering also depends on the support material and the gaseous environment. The dispersion of silver was measured with a number of complementary characterization methods, including H_2-titration, O_2-chemisorption, XRD and TEM. Oxygen causes significant silver sintering on Ag/SiO_2, while the effect is much milder for $Ag/\eta\text{-}Al_2O_3$ and nearly no effect was measured on Ag/TiO_2. Pretreatment in H_2 or He does not affect the silver dispersion on these catalysts. It was also pointed out that once sintered, silver cannot be redispersed by oxygen or chlorine, unlike metals like Pt [18].

Recently, silver catalysts have attracted a lot of attention for potential application in the selective catalytic reduction (SCR) of NO_x by hydrocarbons or oxygenates to remove nitrogen oxides from various exhaust gas effluents [3,4,19–21]. Their promise lies

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in their high activity, high selectivity to dinitrogen, and moderate resistance to H_2O and SO_2. In previous work with Ag-alumina catalysts prepared by the coprecipitation-gelation [19,20], rather unexpectedly, we found that the presence of high concentrations of SO_2 (~1000 ppm) stabilized the catalyst activity for CH_4-SCR of NO at 625 °C and suppressed the catalyst deactivation observed in the absence of SO_2 [21]. In this paper, we further probe the reasons for the observed stability by detailed characterization of Ag-alumina catalysts aged in the absence or presence of SO_2. We also followed the effect of SO_2 on the activity and stability of high-content Ag/Al_2O_3 materials in which part of the silver is present as metallic nanoparticles.

2. Experimental

A coprecipitation-gelation (co-gel) method was used to prepare Ag-alumina catalysts in this work as described in [19]. Low-silver content Ag-alumina catalysts were prepared by leaching out the weakly bound silver on the parent catalysts with a dilute (10%) nitric acid solution [20]. These two types of catalysts are denoted as AlAg(*x*,CG) and AlAg(*x*,L), respectively, where *x* is the wt% of silver, CG stands for coprecipitation-gelation preparation and L for leaching.

Catalytic activity measurements were carried out in a fixed-bed quartz (1 cm I.D.) flow reactor equipped with a K-type thermocouple and a temperature controller, as described elsewhere [19,20]. Specifically, ~0.15 g powder samples were loaded into the reactor, and a feed gas stream containing (mol%) 0.25NO-2CH_4-5O_2-0 or 0.1 SO_2-bal.He at 200 ml/min (GHSV = 50,000 h^{-1}) was introduced. Typically, the reaction took place at 625 °C at atmospheric pressure. At this (or higher) temperature, the catalyst surface is only partially sulfated and active for CH_4-SCR of NO even in the presence of SO_2 in the gas [21]. The reactor effluent was analyzed by a gas chromatograph (HP 5890), which was equipped with a thermal conductivity detector (TCD) and a 10 ft long × 1/8 in. diameter 5A molecular sieve column capable of separating NO, CH_4, O_2, N_2 and CO species. An FTIR (Mattson, Research Series 1), equipped with a 0.75 l/5.6 m gas cell operating at 150 °C, was used to monitor the SO_2 concentration online.

Ag-alumina samples, both fresh and reaction-aged, were examined by HRTEM/EDS on a JEOL 2010 instrument equipped with a LaB_6 electron gun source with a resolution of 0.19 nm. The microscope was operated at 200 kV, and its attached energy dispersive X-ray spectroscopy (EDS) was also used for elemental analysis of selected areas. The sample preparation consisted of suspending the catalyst powders in isopropyl alcohol using an ultrasonic bath and then depositing them onto a carbon-coated 200 mesh Cu grid. Typically, for each sample, the particle size distribution was investigated over many areas of the samples, and representative pictures are shown here.

To identify the crystalline phases, X-ray powder diffraction (XRD) analysis was performed on a Rigaku 300 X-ray diffractometer. Copper Kα radiation was used. The tube voltage was 60 kV, and the current was 300 mA.

TPO (temperature-programmed oxidation) was performed to check for carbon deposition on the Ag-alumina catalysts aged in either of the following two conditions: (1) sulfur-free: 625 °C, 0.25%NO-2%CH_4-5%O_2-He, 24 h; and (2) with sulfur: 625 °C, 0.25%NO-2%CH_4-5%O_2-0.1%SO_2-He, 24 h. Three catalysts, AlAg(6,L), AlAg(10.1,CG) and alumina, were examined. TPO was performed on a Micromeritics Pulse Chemisorb 2705 instrument. Typically, ~0.1 g of aged catalyst was charged into the U-shape sample holder, and 20%O_2/He at 40 ml/min was introduced at RT. Then the sample was heated in this flowing gas mixture to 800 °C at 10 °C/min. Signals of O_2 (32,16), CO(28), CO_2(44,28) and H_2O(18) were monitored by mass spectrometry, as well as some S- or N-containing species: NO(30), NO_2(46), N_2O(44), SO_2(64,48), SO_3(80), H_2S(34), COS(60), CS_2(76) and CH_2S(45). For the MS signal of CO (*m*/*e* = 28), 0.12 of the CO_2 (44) signal was subtracted to account for CO produced by CO_2 cracking in the mass spectrometer ionizer. Similarly, for the *m*/*e* signal of NO (30), 2.7 times the signal of NO_2 (46) was subtracted to account for the NO produced from NO_2 whenever these two components showed up simultaneously.

SO_2 treatment of a pre-sintered Ag-alumina catalyst was conducted to examine whether SO_2 can redisperse silver particles. The sample, AlAg(10.1,CG), was first aged in sulfur-free CH_4-SCR reaction (standard condition: 0.25%NO-2%CH_4-5%O_2) at 625 °C for 24 h. This aged catalyst is denoted as AlAg(10.1,CG)(625C-SCR-24 h). Sulfation of this CH_4-SCR-aged catalyst was performed in a fixed bed quartz flow reactor. Firstly, the sample was heated from RT to 625 °C in He. Then, sulfation was performed in a flow of 516 ppm SO_2/He at 625 °C for specific lengths of time. Finally, the catalyst was cooled down to RT in the same SO_2 gas stream. The gas effluent from the reactor was monitored with a mass spectrometer (Mini-Lab). The sulfated catalyst was examined by TEM (JEOL 2010) and XRD (Philips, X'pert) to determine the dispersion and crystalline phases of silver.

3. Results and discussion

3.1. SO_2-stabilized CH_4-SCR activity of Ag-alumina

A most interesting property of the catalyst in the presence of SO_2 is the stabilization of its activity as we recently reported [21]. Fig. 1 shows this in a cyclic addition/removal of SO_2 over the AlAg(6,L) catalyst. Clearly, addition of SO_2 causes a fast drop in the conversions of NO and CH_4, which are subsequently recovered after removal of SO_2. We have attributed this to reversible adsorption of SO_2 onto the surface sites of Ag-alumina at 625 °C [21]. What is remarkable is the stabilizing effect of SO_2 on the SCR activity of AlAg(6,L), as can be seen in Fig. 1. Under SO_2, both the NO conversion to N_2 and CH_4 conversion to CO_x were stable with time (up to 18 h of time-on-stream). On the contrary, in the absence of SO_2 from the reaction gas mixture, a continuous drop in NO conversion was found. For example, after the last cycle in Fig. 1, when SO_2 was switched off the conversion of NO to N_2 decreased from 82 to 32% in 18 h, while the conversion of CH_4 to CO_x was maintained with time.

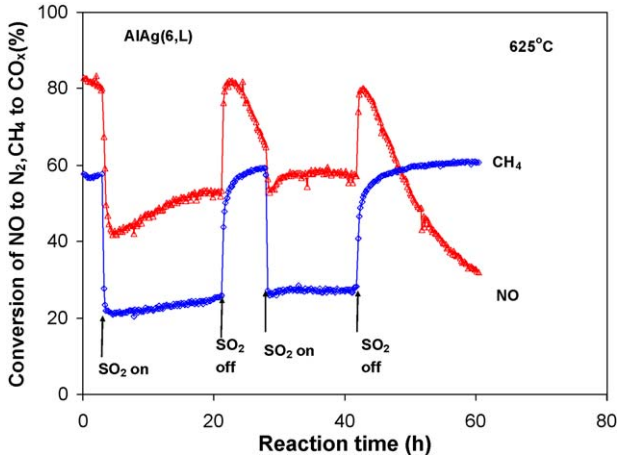

Fig. 1. Effect of SO_2 on the SCR of NO with CH_4 over AlAg(6,L). Catalyst load: 0.15 g. Feed gas: 0.25%NO-2%CH_4-5%O_2-0/1000 ppm SO_2-He, 200 ml/min. *T* = 625 °C. SV = 50,000 h^{-1}.

As a result, the aim of this work was to investigate the role played by potential structural changes of silver on (1) the deactivation of Ag-alumina catalysts in the absence of SO_2; and (2) the enhanced stability of Ag-alumina in the presence of SO_2.

3.2. Deactivation in SO_2-free gas streams

As shown in Fig. 1, the NO conversion to N_2 decreases continuously with time-on-stream in the absence of SO_2. Sintering phenomena (e.g. silver particle growth) or fouling due to carbon deposition are the typical causes of deactivation. We first examined the catalysts for carbon deposition by subjecting them to TPO after they were aged in the absence of SO_2, no carbon deposition was evidenced from the TPO results (not shown) and this deactivation route was ruled out. For comparison, TPO was also performed for a sample aged in the presence of SO_2, and again no evidence for carbon deposition was found.

Catalyst sintering, another common cause of catalyst deactivation, was investigated next. Silver particle sintering is known to occur readily on various supports [5–10]. To examine this, TEM was performed for the Ag-alumina catalysts aged in the absence of SO_2 for various lengths of time, as shown in Fig. 2. Fig. 2(a)–(c) show the TEM of AlAg(7.1,L) aged in CH_4-NO-O_2 at 625 °C for 5, 48 and 60 h, respectively. After reaction for 5 h, small silver nanoparticles of 10–20 nm average size were clear (Fig. 2(a)), indicating destabilization of silver compared to the highly dispersed [Ag-O-Al] species in the fresh sample [20]. With further reaction in the above gas mixture, growth of silver particles became more pronounced, as can be seen in Fig. 2(b) and (c). After 48h-on-stream (Fig. 2(b)), big silver agglomerates reaching

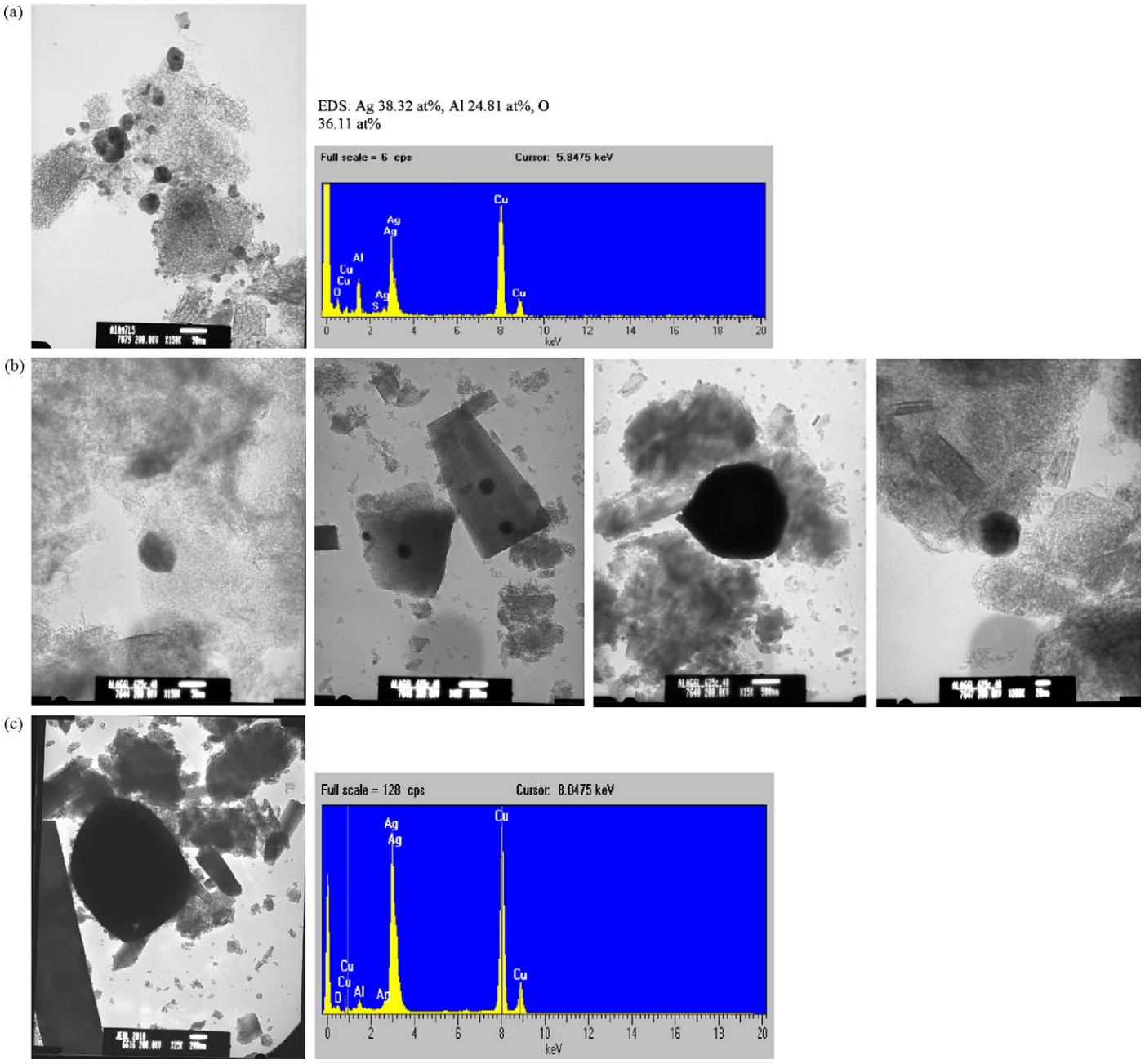

Fig. 2. HRTEM of AlAg(7.1,L) aged in the absence of SO_2. Aging condition: 0.25%NO-2%CH_4-5%O_2-He, 625 °C. Aging time: (a) 5 h; (b) 48 h; (c) 60 h.

micrometer size were observed, together with some smaller silver particles <100 nm. A large clump of silver >1 μm was found after 60 h-on-stream (Fig. 2(c)). These results clearly show severe sintering of silver particles during the CH_4-SCR reaction at 625 °C. Martinez-Arias et al. [22] also reported sintering of silver in Ag/alumina catalysts during C_3H_6-SCR of NO up to 550 °C.

Comparing this data to the NO conversion drop in the absence of SO_2 (Fig. 1), we conclude that the observed deactivation

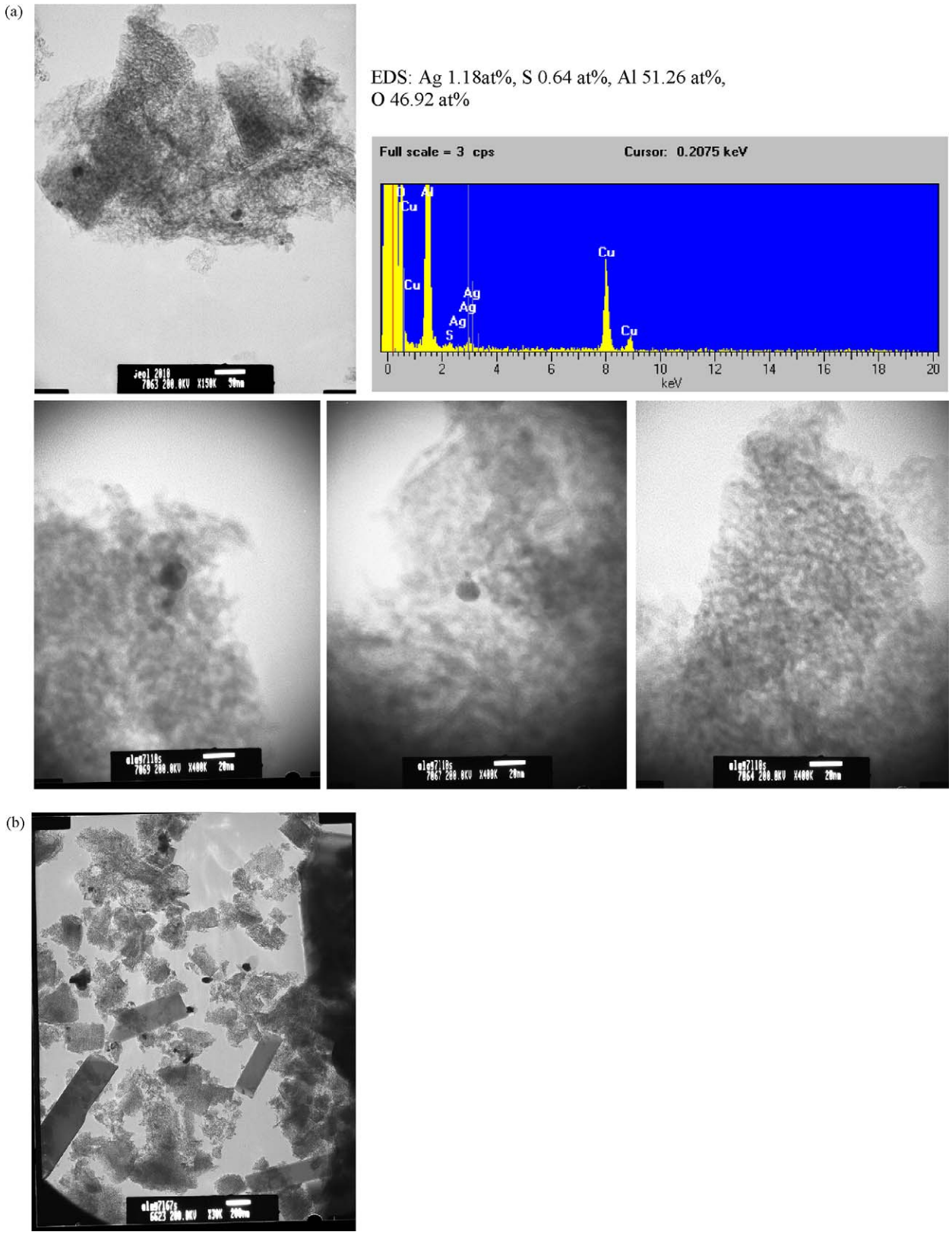

Fig. 3. HRTEM of AlAg(7.1,L) aged in the presence of SO_2. Aging condition: 0.25%NO-2%CH_4-5%O_2-1000 ppm SO_2-He, 625 °C. Aging time: (a) 10 h; (b) 67 h.

is due to silver sintering and hence loss of active sites for the reaction.

3.3. Stabilized structures and performance in the presence of SO_2

HRTEM was also performed with Ag-alumina samples aged in CH_4-NO-O_2-SO_2 for various times, as shown in Fig. 3. Fig. 3(a) and (b) are micrographs of AlAg(7.1,L) aged in CH_4-NO-O_2-SO_2 gas mixtures at 625 °C for 10 and 67 h, respectively. After 10 h, silver was still well dispersed and only a few particles <20 nm were observed, as can be seen in Fig. 3(a). This behavior is in sharp contrast to the case of Fig. 2(a), where the dispersion of silver was drastically lower as evidenced by the appearance of large silver particles after aging for a shorter time in the absence of SO_2. After the 67 h-test (Fig. 3(b)), a few silver particles of ~100 nm size were present, but most silver remained dispersed. This is very different from the severely sintered silver particles (>1 μm, Fig. 2(c)) observed after aging the catalyst in the absence of SO_2. Hence, we conclude that SO_2 plays an important role in suppressing the sintering of silver particles on alumina.

To examine the generality of this stabilization effect of SO_2 on silver structures, we further looked at a high-silver content catalyst, AlAg(10.1,CG), which initially contains silver nanoparticles of 10–20 nm as in Fig. 4(a). As a result of reaction at 625 °C, large silver particles reaching micrometer size were formed on this material after aging in the SO_2-free gas for 24 h (Fig. 4(b)). On the sulfated sample, however, no such severely sintered silver particles were observed, and most of the silver was well dispersed (data not shown). Therefore, the beneficial structural effect of SO_2 also holds for the unleached, high-content AlAg(10.1,CG) sample.

Similar to the activity tests for the leached AlAg(6,L) in Fig. 1, the conversion of NO over AlAg(10.1,CG) decreases with time in the absence of SO_2, while it is maintained at high levels with addition of SO_2, as shown in Fig. 5. For this high-silver content catalyst, there is even an enhanced SCR activity caused by the presence of SO_2, as can be seen by the improved NO conversion to N_2 in Fig. 5. Thus, we next examined the possibility that SO_2 caused redispersion of the particles of silver initially present on the surface which led to this surprising enhanced activity.

3.4. Redispersion of silver particles by SO_2

XRD analyses were used to test the redispersion hypothesis. Fig. 6 shows that metallic silver were present (2θ of 38.2° (1 1 1)

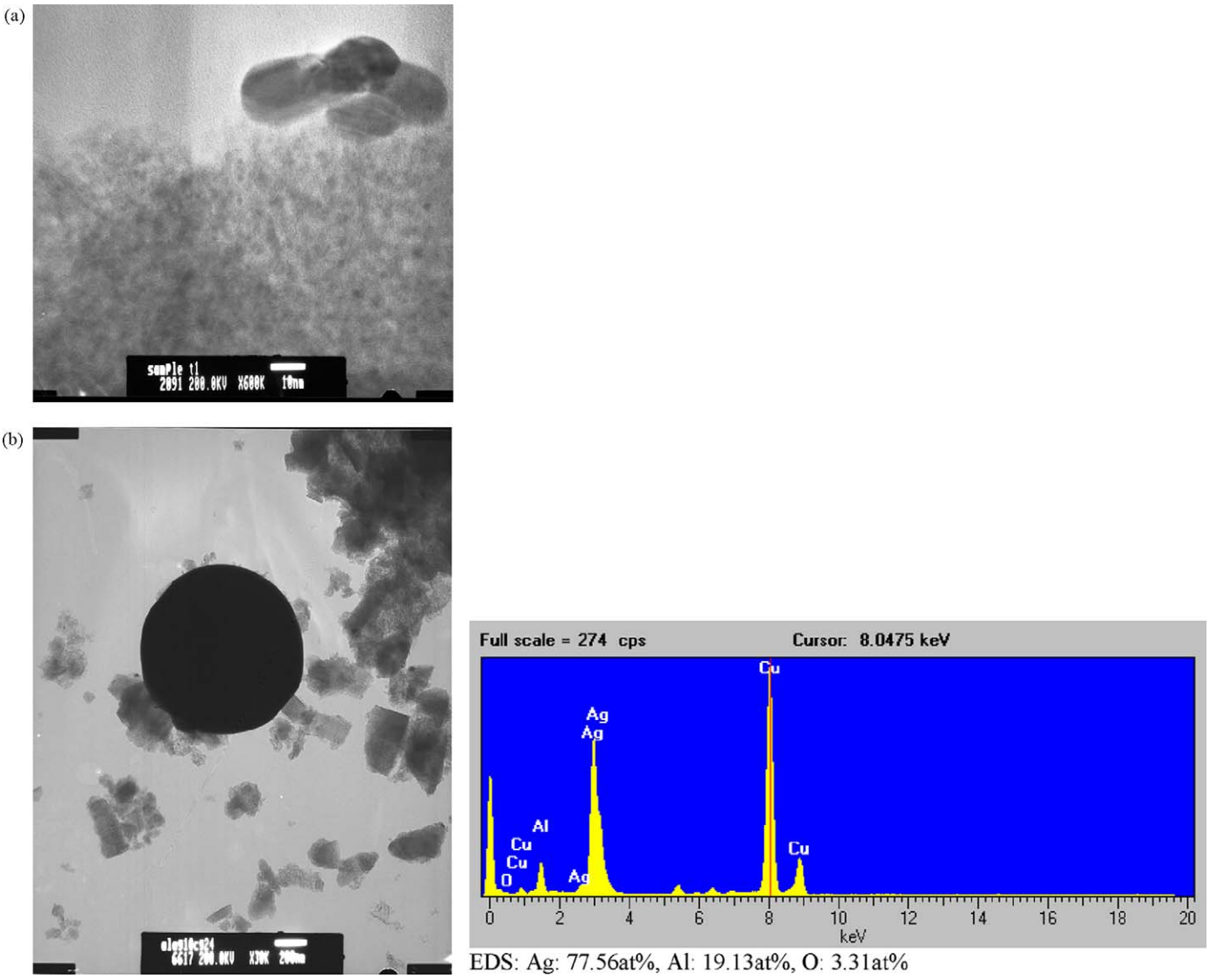

Fig. 4. HRTEM of AlAg(10.1,CG): (a) fresh; (b) aged in the absence of SO_2 (625 °C, 0.25%NO-2%CH_4-5%O_2-He, 24 h).

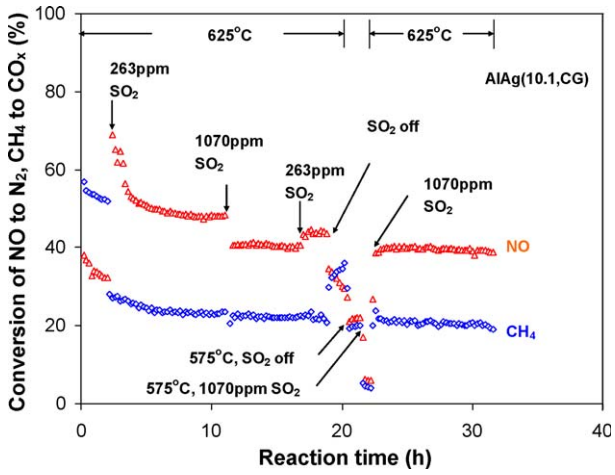

Fig. 5. Effect of SO_2 on the SCR of NO with CH_4 over AlAg(10.1,CG). Catalyst load: 0.15 g. Feed gas: 0.25%NO-2%CH_4-5%O_2-0/263/1070 ppm SO_2-He, 200 ml/min. T = 625 °C.

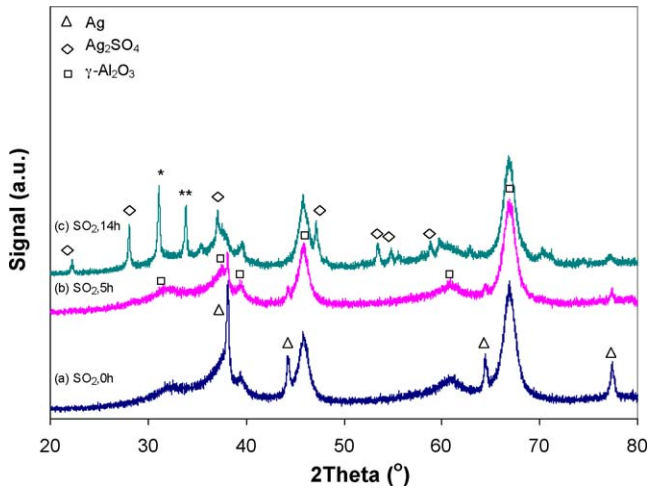

Fig. 8. Time-resolved XRD analysis of AlAg(10.1,CG) (625C-SCR-24 h) upon SO_2 treatment (516 ppm SO_2/He at 625 °C). (a) SO_2, 0 h; (b) SO_2, 5 h (as per Fig. 7a); (c) SO_2, 14 h (as in Fig. 7b). *This diffraction line cannot be unambiguously ascribed to Ag_2SO_4, Al_2S_3, or Al_2O_3, since all three of these have diffraction line at this position. **Diffraction due to Ag_2SO_4 or $Al_2(SO_4)_3$.

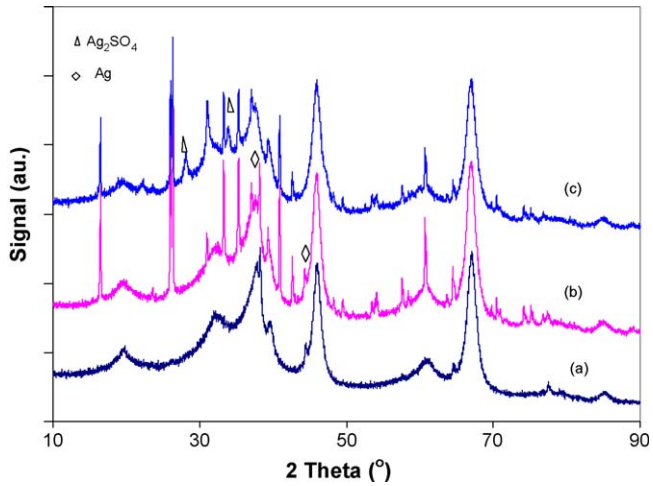

Fig. 6. XRD of aged Ag-alumina catalysts. (a) AlAg(10.1,CG)(625C-SCR-24 h); (b) AlAg(7.1,L)(625C-SCR-60 h); (c) AlAg(7.1,L)(625C-SCR-SO_2-67 h). Aging condition: 0.25%NO-2%CH_4-5%O_2-0/1000 ppm SO_2-He, 625 °C.

and 44.4° (2 0 0)) for two catalysts aged in CH_4-NO-O_2, AlAg(7.1,L)(625C-SCR-60 h) and AlAg(10.1,CG)(625C-SCR-24 h), respectively. Based on Ag(1 1 1), the crystal size of silver on these two catalysts was calculated to be 43.6 and 38.4 nm, respectively. It should be noted that the thus obtained average crystal size by XRD was much smaller than the size of silver agglomerates identified in Fig. 2(c) and Fig. 4(b) by TEM, which could be due to the fact that XRD averages over the entire sample. When the above two catalysts were aged in CH_4-NO-O_2-SO_2 for 24 h at 625 °C, neither metallic silver nor the Ag_2SO_4 phase was identified by XRD. Also shown in Fig. 6, is the XRD pattern of AlAg(7.1,L)(625C-SCR-SO_2-67 h), aged in SO_2 for a longer time, 67 h. No metallic silver phases exist in this sample. Ag_2SO_4 was identified at 2θ of 28.2° and 34.0° and its crystal size was calculated to be 17.8 nm from the peak at 34.0°.

To further probe the hypothesis that the observed SCR activity and stability enhancement of the catalyst is due to SO_2-induced redispersion of silver, we conducted a series of experiments in which a pre-sintered Ag-alumina catalyst, AlAg(10.1,CG)(625C-

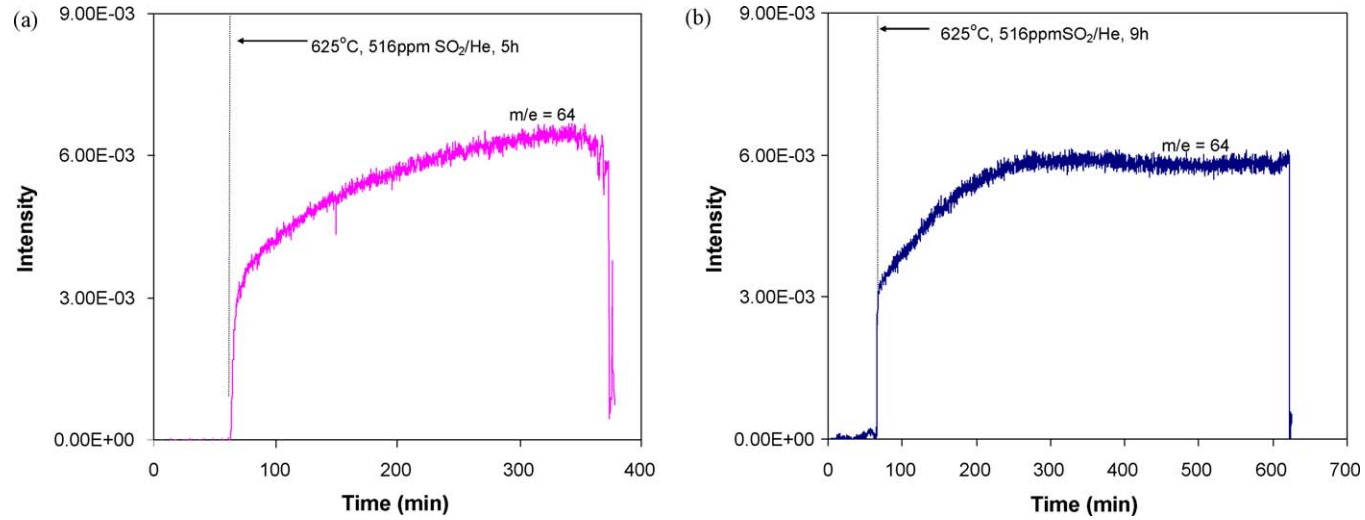

Fig. 7. SO_2 elution monitored by mass spectrometry in two sequential SO_2-treatments (625 °C, 516 ppm SO_2/He) of AlAg(10.1,CG)(625C-SCR-24 h). (a) 5 h; (b) follows (a), 9 h.

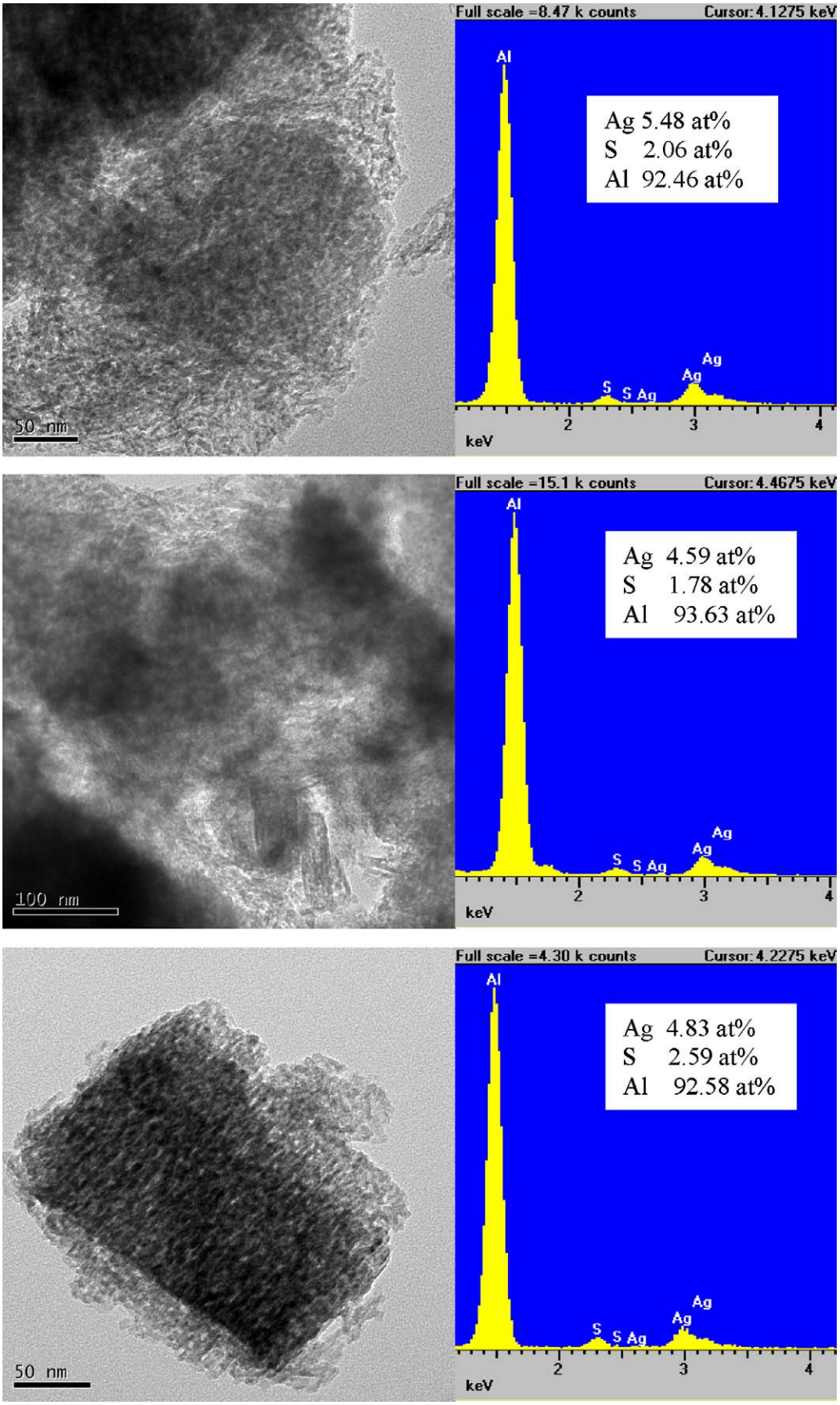

Fig. 9. TEM of AlAg(10.1,CG) (625C-SCR-24 h) treated in SO_2 for 14 h (the sample after treatment in Fig. 7(b); 625 °C, 516 ppm SO_2/He). EDS shows the atomic percentages of each element.

SCR-24 h) was exposed to a flow of SO_2 (516 ppm SO_2/He, at 625 °C). Fig. 7 shows that the concentration of eluted SO_2 gradually increases with time-on-stream, which indicates absorption of SO_2 by the catalyst. The thus "sulfated" sample was characterized by XRD and TEM, as shown in Figs. 8 and 9. Fig. 8(a) shows the XRD results of the starting aged material AlAg(10.1,CG)(625C-SCR-24 h), and strong diffraction lines due to metallic Ag were identified in this catalyst. After being treated in SO_2 for 5 h, the intensity of those diffraction lines diminished drastically, as shown in Fig. 8(b). The metallic silver phase completely disappeared after further 9 h treatment in SO_2 in Fig. 8(c), although Ag_2SO_4 was identified after this extensive treatment in SO_2. Hence, the XRD results strongly support our conclusion that silver particles were redispersed by SO_2. Further, the morphology of the catalyst treated in SO_2 for 14 h was examined by TEM (Fig. 9). No silver particles were identified and silver (sulfur-bounded) was well dispersed as indicated by the EDS analysis.

It is noteworthy that the saturation of the aged catalyst by SO_2 takes on the order of 1–3 h as can be seen in Fig. 7. However, the redispersion of silver may have faster dynamics, when the starting sample contains smaller silver particle sizes, and when exposures occur at higher concentrations of SO_2 as manifested by the relatively fast cyclic performance in Figs. 1 and 5.

To the best of our knowledge, this is the first report for a stabilization of silver on alumina surfaces by SO_2 under SCR of NO_x at temperatures exceeding 600 °C.

At the present time we do not have a satisfactory model on how SO_2 stabilizes and redisperses silver species on the Ag-alumina catalyst during CH_4-SCR of NO_x at temperatures above 600 °C. But our data consistently show that SO_2 adsorbs reversibly on Ag-alumina under these reaction conditions [21]. Tentatively, therefore, we propose that the adsorbed SO_2 can either change the bonding environment of the alumina surface and hence the bonding strength of Ag atoms [12] or form Ag–SO_x bonds that inhibit migration of silver. Along the same line, carbon deposition on silver particles by heating in C_2H_4 has been reported to prevent silver from sintering [9,10]. Wang et al. [23] reported much slower nucleation of FePt particles on FePt/ZnS/SiO_2 than on FePt/SiO_2, and the particle size was also much smaller in the former case. The authors explained this by the formation of Fe–S and Pt–S bonds on ZnS, which results in increased activation energies for diffusion and aggregation of FePt particles [24]. From both a mechanistic and a practical viewpoint, understanding how the stabilization of silver in dispersed state comes about by SO_2 warrants further investigation. Furthermore, how SO_2 can disperse already formed particles of silver on alumina at temperatures exceeding 600 °C remains an open question at the present time.

4. Conclusion

The previously reported SO_2-derived stability of Ag-alumina catalysts for SCR of NO with methane at high temperatures (>600 °C) was further investigated in this work. A beneficial structural effect of SO_2 on silver is reported for the first time. In the absence of SO_2, severe sintering of silver takes place in the reaction gas at 625 °C and silver agglomerates into large clusters of μm size. However, the presence of SO_2 keeps the silver species in a dispersed state on alumina and suppresses deactivation. Further, we found that SO_2 redisperses already formed silver particles on a reaction-aged silver-alumina surface at 625 °C. As a consequence, the SCR activity of high-content Ag/Al_2O_3 can be tuned to higher values by addition of SO_2, as the silver particles disappear and silver dispersion is increased. These findings are important for the treatment of engine exhaust gases containing residual sulfur.

Acknowledgements

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